REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER (14) TR-7	2. GOVT ACCESSION NO. AD-A093 285	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) Hydrogenation of CO on Alumina Supported Metals: A Tunneling Spectroscopy Study		5. TYPE OF REPORT & PERIOD COVERED Technical Report
		6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) R. M. Kroeker, P. K. Hansma and W. C. Kaska		8. CONTRACT OR GRANT NUMBER(s) N00014-78-C-0011 NSF-DMR 77-2743
9. PERFORMING ORGANIZATION NAME AND ADDRESS Department of Chemistry; Department of Physics Quantum Institute, University of California, Santa Barbara, CA 93106		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS NR056-6731
11. CONTROLLING OFFICE NAME AND ADDRESS Office of Naval Research Department of the Navy Arlington, VA 22217		12. REPORT DATE
		13. NUMBER OF PAGES
14. MONITORING AGENCY NAME & ADDRESS(if different from Controlling Office)		15. SECURITY CLASS. (of this report) Unclassified
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

LEVEL

16. DISTRIBUTION STATEMENT (of this Report)

Approved for public release and sale; distribution unlimited.

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

18. SUPPLEMENTARY NOTES

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Carbon monoxide, rhodium, Cobalt, nickel, H_2, CO^- adsorption with CO, tunneling spectroscopy, vibrational spectroscopy.

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

DD FORM 1473 EDITION OF 1 NOV 65 IS OBSOLETE
1 JAN 73
S/N 0102-LF-014-6601

Hydrogenation of CO on Alumina Supported Metals:
A Tunneling Spectroscopy Study

by

R. M. Kroeker, W. C. Kaska and P. K. Hansma

80 12 24 010

HYDROGENATION OF CO ON ALUMINA SUPPORTED METALS;
## A TUNNELING SPECTROSCOPY STUDY

R.M.Kroeker
I.B.M. Research Laboratory
5600 Cottle Road, San Jose, California 95193

P.K.Hansma and W.C.Kaska
Department of Physics (PH) and Department of Chemistry (WK)
University of California, Santa Barbara, California 93106

Introduction

The hydrogenation of CO on alumina supported metals has been the subject of many research efforts. This report is about the application of a relatively new technique, tunneling spectroscopy, to the problem of identifying the reaction intermediates that are formed on the catalyst surface. Tunneling spectroscopy is a vibrational spectroscopy that presents information about the system being studied in much the same way as do infrared and raman spectroscopy. The selection rules of tunneling are very weak; the spectrum observed consists of both the infrared and raman allowed vibrations. This similarity between techniques invites comparison of the results obtained in this work with those of previous infrared studies, such as those done by G.Blyholder, et al.(1), and R.A.Dalla Betta, et al.(2). From such comparisons it is possible to say that all three techniques find the observation of submonolayers of hydrocarbons to be technically demanding. No experimental method is yet available that allows the complete determination of all reaction pathways on a catalyst surface. As a first step toward this ultimate goal we report the observation of the hydrogenation of CO chemisorbed on alumina-supported metal particles with tunneling spectroscopy.

Inelastic Electron Tunneling Spectroscopy (IETS) measures the energies, and thus the frequencies, of the normal modes of vibration of molecules that are incorporated in order near the insulator of a metal-insulator-metal tunnel junction. In this work all junctions are made with an aluminum-aluminum oxide-dopant-lead structure, where the dopant consists of small metal particles (with 10-40 Angstrom diameters) that are exposed to CO and hydrogen. The insulator plus dopant thickness is approximately 30 Angstroms, thin enough to allow electrons to tunnel from the aluminum to the lead electrode whenever a voltage (aluminum negative) is applied. The maximum energy of a tunneling electron above the fermi energy of the lead electrode is the energy it gains from the applied voltage, eV. Experimentally it is found that these tunneling electrons can excite the vibrations of molecules in or near the insulating barrier. The dominant criterion
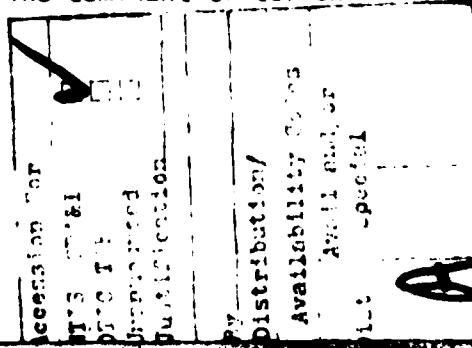
is simply that the electron must have an energy greater or equal to the vibrational energy, $h\nu$, of the molecule excited. This gives rise to a threshold voltage, $V = h\nu/e$, that can be observed as a conductance increase. This increase is then measured and displayed in a form comparable to the absorbence in an infrared experiment. A more detailed description of the experimental techniques of tunneling can be found in the review literature ([3]).

Rhodium

The top trace in Figure 1 shows the spectrum obtained for CO chemisorbed on rhodium particles. This differential spectrum is the result of subtracting the signals from two junctions; one prepared with rhodium particles, and another without rhodium particles. The resulting differential spectrum clearly shows vibrations due to the chemisorbed CO at 413, 465, 600, 1721, and 1942 cm^{-1}. The exact frequencies measured depend on the particle size, the temperature of the junction during formation, the degree of surface coverage, and the amount of other gases (such as water) chemisorbed on the surface. Detailed studies of these small shifts (typically a few percent) have not been completed. A recent study of such shifts due to temperature has been published by P.R.Antoniewicz, et al. using infrared spectroscopy ([4]). Structure due to the aluminum oxide, aluminum, and lead electrodes is greatly suppressed. The CO is chemisorbed as three different species on the rhodium surface ([5],[6],[7]). Three species have also been observed with infrared spectroscopy on similar systems. The identification of the three types of chemisorbed CO by infrared workers ([8],[9],[10],[11]) as a gem dicarbonyl, $Rh(CO)_2$, a linear species, $RhCO$, and a multiply bonded species, Rh_xCO, agrees with the tunneling identifications derived from isotopic shifts. In tunneling spectra the dicarbonyl species is best seen by observing a low frequency bending mode at 413 cm^{-1}, the linear species can be identified by a low frequency bending mode at 465 cm^{-1}, and the multiply bonded species can be identified by the presence of the CO stretching vibration at 1721 cm^{-1}. The broad band at 600 cm^{-1} contains the rhodium-carbon stretching vibrations for all three species, and the CO stretching mode at 1942 cm^{-1} contains contributions from both the linear and dicarbonyl species.

The lower trace in Figure 1 shows the results of heating the tunnel junctions (complete with a lead top electrode) in a high pressure cell with hydrogen. It is seen that the CO reacts with the hydrogen to produce hydrocarbons on the rhodium particles. Studies with isotopes and comparison of mode positions with model compounds identify the dominant hydrocarbon as an ethylidene species ([12]). The importance of this observation is obviously not that CO and hydrogen react on rhodium to produce hydrocarbons, but that they will do so in a tunneling junction in a way so that the reaction can be observed. The hydrocarbon is seen as it forms from the chemisorbed monolayer of CO (verified by isotopes). As

it forms without the presence of gas phase CO, and no surface species containing oxygen is observed, it seems unlikely to be formed by CO insertion. A possible mechanism would be the polymerization of CH_2 groups from dissociated CO that had been hydrogenated. At any rate, the ethylidene species is a relatively stable surface species when CO is hydrogenated on rhodium particles that are incorporated in tunneling junctions. At present, it is not known if this same species is formed on supported rhodium particles in a more conventional reaction cell. It is not known because no other technique has developed the technology needed to observe the formation of the first submonolayer of hydrocarbons on supported metals. A similar species has been observed to form on single crystal rhodium from the chemisorption of ethylene (13,14). It is to be expected that future work will allow direct comparisons of surface species formed by different techniques, but until this is possible questions raised by the presence of the top lead electrode in these tunneling experiments can not be answered.

Cobalt

Figure 2 shows the differential spectra of CO chemisorbed on supported cobalt particles both before and after heating in hydrogen. Again it is seen that the chemisorbed CO reacts with hydrogen that diffuses through the lead electrode to form hydrocarbons in the tunneling junction. For the case of cobalt much less is known about the nature of the chemisorbed CO and the type of hydrocarbon formed. This information should become available as soon as we do the extensive work with isotopes necessary to identify the species involved. It is clear, however, that the hydrocarbon formed on cobalt is different from that formed on rhodium. The cobalt related species has vibrations near 1600 and 760 cm^{-1} that the rhodium related species does not have. The mode near 1600 cm^{-1} should involve oxygen, and this can be tested with isotopes. As mentioned above, the rhodium species does not contain oxygen. The mode near 760 cm^{-1} possibly is due to CH_2, a group that also does not appear in the rhodium species. Thus even before this species is identified, it is clear that the reaction pathway for hydrogenation of CO on cobalt is distinct from that on rhodium. This is, of course, no surprise; it has long been known that each metal has its own product distribution and reaction kinetics when used as a catalyst. What is noteworthy is that tunneling spectroscopy has been able to model supported catalysts well enough to reflect this difference between different metals. This suggests that whatever the effect of the lead electrode is on these reactions, there is information to be had from comparisons between the reactions of different metals under the same conditions.

Figure 3 shows the results obtained to date on the hydrogenation of CO chemisorbed on supported iron particles. Iron is a difficult metal to work with in tunneling junctions due to its magnetic properties. We have developed a technique (15) that allows us to obtain spectra of highly dispersed iron with chemisorbed CO, as shown in the lower trace in the figure. Isotopic shift experiments indicate the CO is chemisorbed with predominantly linear character. The spectrum contains two bending modes at 436 and 519 cm^{-1}, and two stretching modes at 569 and 1856 cm^{-1}. When these junctions are heated in hydrogen, some hydrocarbon is seen to form. At present, we are unable to identify the species formed due to a lack of intensity. As we heat the junctions the particles become magnetic, as evidenced by the rise of the background with heating shown in the middle and upper traces in the figure. This could be due to the sintering of the particles or due to the loss of chemisorbed CO. All our attempts to increase the intensity of the hydrocarbon modes formed during heating have been foiled by this background structure. While we expect to be able to overcome this difficulty with continued effort, at present all that can be learned about this hydrocarbon species is that it also exhibits a mode near 1600 cm^{-1} that can be expected to involve oxygen. This implies that the reaction pathway on iron more closely follows that of cobalt than that of rhodium, a fact that can also be derived from many different experiments and processes with commercial catalysts (16).

Nickel

Nickel is known for its selectivity for methanation. This selectivity for methane implies a lack of carbon-carbon bonding on the metal surface when compared to cobalt or rhodium. Figure 4 shows our results for the hydrogenation of chemisorbed CO on supported nickel particles. The CO is chemisorbed on the nickel in at least four different ways (17). Upon heating in hydrogen the CO reacts and/or desorbs forming very little surface hydrocarbon. We feel this lack of surface hydrocarbon reflects the selectivity of alumina supported nickel particles for the formation of methane. The modes that are seen to form are again too weak for identification, as was the case for iron. We expect that future work with nickel will improve the observed signal to noise ratio significantly. It should be remembered that tunneling spectroscopy is less than twenty years old; its application to studies of the activation of CO is less than five years old. With this first work with supported metal particles we hope to have demonstrated some of the potential tunneling spectroscopy for the modelling of adsorption and reaction on catalist surfaces.

Acknowledgments

Literature Cited

1. Blyholder,G.; Neff,L.D., J. Phys. Chem., 1962, 66, 1664-1667.
2. Dalla Betta,R.A.; Shelef,M., J. Catal., 1977, 48, 111-119.
3. Hansma,P.K., Phys. Rep., 1977, 30C, 145-206.
4. Antoniewicz,P.R.; Cavanagh,R.R.; Yates,J.T.Jr., J. Chem. Phys., 1980, 73, 3456-3459.
5. Hansma,P.K.; Kaska,W.C.; Laine,R.M., J. Amer. Chem. Soc., 1976 98, 6064-6065.
6. Kroeker,R.M.; Kaska,W.C.; Hansma,P.K., J. Catal., 1979, 57, 72-79.
7. Kroeker,R.M.; Kaska,W.C.; Hansma,P.K., J. Catal., 1980, 63, 487-490.
8. Yang,A.C.; Garland,C.W., J. Phys. Chem., 1957, 61, 1504-1512.
9. Arai,H.; Tomanaga,H., J. Catal., 1976, 43, 131-142.
10. Yao,H.C.; Rothschild,W.G., J. Chem. Phys., 1978, 68, 4774-4780.
11. Yates,J.T.; Duncan,T.M.; Worley,S.D.; Vaughan,R.W., J. Chem. Phys., 1979, 70, 1219-1224.
12. Kroeker,R.M.; Kaska,W.C.; Hansma,P.K., J. Catal., 1980, 61, 87-95.
13. Ibach,H.; Hopster,H.; Sexton,B., Appl. Sur. Sci., 1977, 1, 1-24.

14. Kesmodel,L.L.; Dubois,L.H.; Somerjai,G.A., Chem. Phys. Lett., 1978, 56, 267-271.

15. Kroeker,R.M.; Kaska,W.C.; Hansma,P.K., J. Chem. Phys., 1980, 72, 4845-4852.

16. Mills,G.A.; Steffgen,F.W., Catal. Rev., 1973, 8, 159-210.

17. Kroeker,R.M.; Kaska,W.C.; Hansma,P.K., J. Chem. Phys., 1980, in press.

Figure Captions

Figure 1. Differential spectra of CO chemisorbed on alumina supported rhodium particles before and after heating to 420 K in hydrogen. One of the three species of chemisorbed CO remains after heating and can be identified by a bending mode at 478 cm^{-1}, a stretching mode at 586 cm^{-1}, and a stretching mode at 1937 cm^{-1} as a linear CO species. The other CO species react and/or desorb while producing hydrocarbons on the rhodium particles. The dominant species formed has been identified as an ethylidene species.

Figure 2. Differential spectra of CO chemisorbed on alumina supported cobalt particles both before and after heating in hydrogen to 415 K. The chemisorbed CO is seen to react and form hydrocarbons in the tunnel junction. This hydrocarbon species is distinct from that formed on rhodium as seen by vibrational modes near 1600 cm^{-1} and 760 cm^{-1}.

Figure 3. Differential spectra of CO chemisorbed on alumina supported iron particles shown before and after two heatings in hydrogen to 420 K. Some CO reacts to form hydrocarbons on the iron particles. The rising background seen at low frequencies indicates the formation of magnetic particles, either through sintering or the desorption of CO. The formation of OH in the junction upon heating does not correlate with the formation of a carbon-oxygen bond nor with the formation of the carbon-hydrogen bonds.

Figure 4. Differential spectra of CO chemisorbed on alumina supported nickel particles both before and after heating to 425 K. Very little surface hydrocarbon is seen to form on the nickel particles. This lack of surface hydrocarbon reflects the selectivity of such catalysts for methanation over Fisher-Tropsch synthesis.

INTENSITY (100 nV PER DIV.)

CO ON NICKEL/ALUMINA
HEATED TO 425K IN H₂

CO ON IRON/ALUMINA
HEATED TO 420 K IN H_2 + CO

CO ON COBALT/ALUMINA
HEATED TO 415K IN H_2

INTENSITY (100 nV PER DIV.)

x1

x2

meV

cm^{-1}

INTENSITY (100 nV PER DIV.)

CO ON RHODIUM/ALUMINA
HEATED TO 420K IN H₂